Report to the

MASSACHUSETTS BAYS PROGRAM

BIOAVAILABILITY AND BIOTRANSFORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN BENTHIC ENVIRONMENTS OF COASTAL MASSACHUSETTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS FOR RESOURCE MANAGEMENT

Prepared by

Anne McElroy*
Environmental Sciences Program
University of Massachusetts-Boston

Michael Shiaris
Biology Department
University of Massachusetts-Boston

Judith McDowell Capuzzo
Brian Howes
John Molongoski
Biology Department
Woods Hole Oceanographic Institution

*Current Address:
New York Sea Grant Institute
115 Nassau Hall
State University of New York at Stonybrook
Stony Brook, NY 11794-5001

NOVEMBER 3, 1994

MBP-95-02S

Funded by: The Massachusetts Environmental Trust

EXECUTIVE SUMMARY
AND RECOMMENDATIONS FOR RESOURCE MANAGEMENT

BIOAVAILABILITY AND BIOTRANSFORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN BENTHIC ENVIRONMENTS OF COASTAL MASSACHUSETTS

Anne E. McElroy*
University of Massachusetts-Boston
Environmental Sciences Program

Michael Shiaris
University of Massachusetts-Boston
Biology Department

John Molongoski
Brian Howes
Judith McDowell Capuzzo
Biology Department
Woods Hole Oceanographic Institution

Prepared for the Massachusetts Bays Program
November 1994

* Current address: New York Sea Grant Institute, SUNY Stony Brook, Stony Brook, NY 11794

This research was made possible by funding from The Massachusetts Environmental Trust - an environmental philanthropy focussing on the Commonwealth's coastal resources.

MASSACHUSETTS BAYS PROGRAM

100 Cambridge Street, Room 2006, Boston, Massachusetts 02202 (617) 727-9530 *fax (617) 727-2754*

FOREWORD

The roots of the Massachusetts Bays Program extend back to 1982, when the City of Quincy filed suit against the Metropolitan District Commission and the Boston Water and Sewer Commission over the chronic pollution of Boston Harbor, Quincy Bay, and adjacent waters. Outdated and poorly maintained sewage treatment plants on Deer Island and Nut Island were being overwhelmed daily by sewage from the forty-three communities in the Metropolitan Boston area. Untreated and partially treated sewage were spilling into Boston Harbor.

Litigation over the pollution of Boston Harbor culminated in 1985 when the United States Attorney filed suit on behalf of the Environmental Protection Agency against the Commonwealth of Massachusetts for violations of the Federal Clean Water Act. The settlement of this suit resulted, in 1988, in the creation of the Massachusetts Water Resources Authority, the agency currently overseeing a multi-billion dollar project to repair and upgrade Metropolitan Boston's sewage treatment system. In addition, the settlement resulted in the establishment of the Massachusetts Environmental Trust - an environmental philanthropy dedicated to improving the Commonwealth's coastal and marine resources. $2 millon in settlement proceeds were administered by the Trust to support projects dedicated to the restoration and protection of Boston Harbor and Massachusetts Bay.

The Trust provided $1.6 million to establish the Massachusetts Bays Program, a collaborative effort of public officials, civic organizations, business leaders, and environmental groups to work towards improved coastal water quality. The funding was used to support both a program of public education and a scientific research program focusing on the sources, fate, transport and effects of contaminants in the Massachusetts and Cape Cod Bays ecosystem. To maximize the efficiency of limited research funding, the sponsored research program was developed in coordination with research funded by the MWRA, the United States Geological Survey, and the Massachusetts Institute of Technology Sea Grant Program. The study described in this report addresses the bioavailability of polycyclic aromatic hydrocarbons in the sediments of Boston Harbor and less contaminated areas of Massachusetts Bay to benthic organisms, as well as the potential for food chain transfer to commercially important species. This information is helping to meet the Massachusetts Bays Program goal of producing an area-wide management plan for water quality enhancement and protection. In addition, the study has provided a basis for identifying data gaps to be addressed through additional research.

In April, 1990, following a formal process of nomination, the Massachusetts Bays Program became part of the National Estuary Program. The additional funding provided as part of this joint program of the Environmental Protection Agency and the Commonwealth of Massachusetts is being used to continue a coordinated program of research in the Massachusetts Bays ecosystem, as well as supporting the development of a comprehensive conservation and management plan for the coastal and marine resources of Massachusetts and Cape Cod Bays.

The information in this document has been subject to Massachusetts Bays Program peer and administrative review and has been accepted for publication as a Massachusetts Bays Program document. The contents of this document do not necessarily reflect the views and policies of the Management Conference.

The Massachusetts Bays Program is sponsored by the Massachusetts Executive Office of Environmental Affairs through the Coastal Zone Management Office and the U.S. Environmental Protection Agency, Region I, John F. Kennedy Federal Building, Boston, MA 02203.

I. Historical Context and Goals of Project

Polycyclic aromatic hydrocarbons (PAHs) comprise a ubiquitous class of organic contaminants distributed world-wide through the use of fossil fuels for energy. Because of the hydrophobic properties of individual PAHs, these contaminants readily sorb to particles. Thus, once introduced to aquatic systems, PAHs become associated with sediment deposits and may be readily accumulated by benthic organisms. Transfer of PAHs to marine biota and the human consumer and toxicological effects on the ecosystem are dependent on the availability and persistence of these contaminants within benthic environments.

Concentrations of total PAHs in Boston Harbor sediments are among the highest reported for all coastal sites of the United States (MacDonald, 1991). Among sites examined within the New England region, concentrations of total PAHs in sediment samples from Boston Harbor exceeded concentrations in samples from other sites by as much as one to two orders of magnitude (MacDonald 1991). A recent survey of records of organic contamination in Boston Harbor, and Massachusetts Bays found concentrations of two PAHs (benzo[a]pyrene and phenanthrene) to exceed proposed sediment quality criteria in Boston Inner Harbor, Dorchester Bay, and two offshore sites including the planned MWRA outfall site and the Massachusetts Bay dump site (Cahill and Imbalzano 1991).

Biota from Boston Harbor have also been found to be highly contaminated; concentrations of total PAHs in samples of the blue mussel (*Mytilus edulis*) from the NOAA National Status and Trends Program are within the upper 15% of the most contaminated sites from the U.S. coastline. An understanding of the fate and effects of PAHs in Boston Harbor sediments is critical if we are to define the potential threat to marine biota and the human consumer and if we are to predict the extent to which harbor sediments will continue to be a source of PAHs to the benthic ecosystems of Massachusetts Bay. The analyses done to date of the loadings of PAHs into the water of Boston Harbor and Massachusetts Bays have not included sediments as a source (Menzie-Cura & Associates 1991).

Project Goals:

The overall objectives of this project were to:

(1) assess the bioavailability of PAHs in sediments from Boston Harbor and less contaminated areas of Massachusetts Bay to benthic organisms; and

(2) assess the role of metabolism in controlling bioavailability of PAHs, persistence of PAHs in surficial sediments, flux of PAHs to the water column, and the potential for food chain transfer of PAHs to commercially important species.

Methods:

These assessments were done in four sediment types ranging in organic carbon content from 1.7 to 8.9%. Two sediments were collected from Boston Harbor (Spectacle Island and Fort Point Channel), and two from less urbanized areas of coastal Massachusetts (Little Pond, and Buzzards Bay)(Figure 1). Using flow-through microcosms, aerobic and anaerobic microbial activity was assessed before and after the addition of two PAHs, benzanthracene and phenanthrene. The fate of the PAHs was followed before and after the addition of suspension feeding polychaete worms *Scolecolepides (=Marenzellaria) viridis*, and suspension feeding clams *Mya arenaria*. The fate of added PAHs and their metabolites was measured in the sediment, in the water column and in macrofauna.

Results:

Sediment characteristics and microbial activity

Sediments from Little Pond had the highest organic carbon content (8.9%), followed by Fort Point Channel (4.7%), Spectacle Island (2.3%), and Buzzards Bay (1.7%) sediments. Aerobic microbial activity as measured by whole sediment oxygen consumption, anaerobic microbial activity, as measured by sulfate reduction in sediments, generally followed the similar patterns although the ranking of Fort Point Channel and Spectacle Island tended to be reversed. This was probably due to a period of elevated temperature due to loss of temperature control during the power outages caused by Hurricane Bob during the Spectacle Island experiment.

A summary of average redox profiles observed in each sediment is presented in Figure 2. Sediments from Little Pond and Spectacle Island became reduced at the shallowest depths (approx. 15 mm), followed by Fort Point Channel sediments (approx. 35 mm), with Buzzards Bay sediments remaining oxidized almost to the base of the sediment column (80 mm).

PAH in sediments

Greater than 93 and more commonly 97% of radioactivity recovered from sediment extracts was still present as parent compound. Only minimal evidence of complete breakdown of benzanthracene to carbon dioxide was observed in sediments (<1% of total activity), and then primarily in sediments from Boston Harbor. Significantly more phenanthrene was degraded to carbon dioxide (0.6 to 12% of total activity). In this case no clear correspondence to either location or carbon content was observed. The relative percentage of conversion between phenanthrene and benzanthracene is shown in Figure 3.

Flux of PAH from Sediments in Water

Total PAH-derived material removed to the water column was similar for benzanthracene and phenanthrene, and for three out of four sediment types. Flux from

Buzzards Bay, Little Pond, and Spectacle Island sediments averaged 4.3 nmole/m ^{2}-day, while average flux from Fort Point Channel sediment was two orders of magnitude higher, 672 nmole/m ^{2}-day. In all cases greater than 50 % of material collected on XAD cartridges was present as some form of PAH metabolite. Material removed from Fort Point Channel Sediments was the most extensively metabolized.

Metabolism and microbial degradation of PAHs appear to contribute significantly to the flux of PAHs from harbor sediments. Organic carbon concentration of the sediment was not found to be a good predictor of flux. Turnover times for individual compounds varied significantly (Figure 4). Phenanthrene was degraded very rapidly, with calculated mean turnover times ranging from 10 to 50 days. In contrast, relatively slow degradation was observed for benzanthracene with calculated mean turnover times ranging from 200 to 800 days. These experiments provide empirical evidence of the importance of biological processes in controlling PAH bioavailability and turnover in Boston Harbor sediments. Estimates of PAH flux from harbor sediments must consider the contribution of such processes to adequately assess the fate of PAHs in Massachusetts Bay.

Bioaccumulation of PAH into macrofauna

The deposit-feeding polychaete worm *Scolecolepides viridis* accumulated more phenanthrene and benzanthracene than the suspension feeding clam *Mya arenaria*. In addition, worms rapidly metabolized the PAHs. Metabolites accounted for more than 50% of the total body burdens of PAH measured. Bioaccumulation factors for PAH-derived material measured in these experiments ranged from 0.02 to 0.11 for clams, and 0.4 to 2.7 for worms. These values can be used to predict tissue concentrations and trophic transfer of PAHs based on sediment concentrations (Table 1).

In summary, sediment organic carbon did not appear to be the primary factor controlling bioaccumulation, flux, or metabolism of PAHs in the coastal sediments tested. Microbial metabolism and mineralization of PAHs did not appear to be directly correlated to overall aerobic or anaerobic microbial activity in these sediments, although in most cases the addition of phenanthrene stimulated microbial activity. While phenanthrene was more susceptible to microbial metabolism than benzanthracene, worms metabolized both PAH to a similar extent. The deposit-feeding worms accumulated both PAHs more extensively than suspension feeding clams. Under the conditions employed in these experiments, macrofauna did not have a consistently significant impact on release of PAH from sediments. Most PAH-derived material removed from the sediments was metabolized.

II. Relevance to Resource Management Concerns

PAH contamination of marine biota poses risks to both ecological systems and human health. Although there are no Food and Drug Administration guidelines for PAH levels in seafood, there is growing concern that the presence of PAHs in tissues of marine biota may pose significant human health risks because of the carcinogenic and mutagenic nature of individual PAHs. The extent of the problem in Boston Harbor and Massachusetts Bay has not been quantified but the relatively high ranking of Boston Harbor with respect to PAH sediment contamination certainly warrants careful investigation of the relative ecological and human health risks associated with this high level of PAH contamination. Although general trends in PAH contamination have been defined (e.g., higher concentrations of total PAHs in the inner harbor of Boston, lesser concentrations with distance from the inner harbor), critical information on the behavior and effects of individual compounds is lacking. If harbor sediments continue to be a major source of PAHs to the Massachusetts Bay ecosystem, even with the improvement in water quality from the reduction of point source PAH contamination, the potential risks to both marine biota and the human consumer must be defined.

To better understand the fate and potential effects of PAHs in Boston Harbor and Massachusetts Bay, the following parameters need to be evaluated:

1. Define the sources of contamination for specific PAHs - what is the relative contribution of different point and non-point sources to loading of individual compounds? An inventory of every compound is not feasible but an assessment of compounds representative of different compounds classes such as benzanthracene or benzo[a]pyrene for the higher molecular weight PAHs and phenanthrene for the more biodegradable PAHs should be possible.

2. Determine the persistence, degradation rates, and biogeochemical cycling of specific PAHs in sediments along a gradient from the inner harbor to Massachusetts Bay. Analysis of pore water colloidal material should be conducted to better characterize sorptive capacity of the sedimentary environment. How does the flux of specific compounds, sediment and pore water concentrations, and the body burdens of resident organisms vary with site?

3. Determine the tissue concentrations of individual PAHs in representative species of fish and shellfish, collected along a gradient from the inner harbor to Massachusetts Bay. Representative species should be chosen with regard to their mode and location of feeding, their importance in either the human or aquatic food chain, and their ability to metabolize PAHs.

4. On a population basis, using similar species during seasons with limited migrations, define patterns of contaminant exposure and the relationship between exposure and changes in physiological condition or other parameters of biological change. The results of these studies should be used in the determination of sediment quality criteria.

Such a program could lead to a better understanding of the causal relationship between input of specific PAHs and the relative ecological and human health risks associated with such inputs.

III. Future Studies

Sediment organic carbon alone cannot be used as a good predictor of bioaccumulation, flux or susceptibility to metabolism of sediment-bound PAHs in fine coastal sediments. Other factors, possibly the presence of other contaminants or amounts of dissolved organic carbon matter available, are having a bigger influence. For PAHs, which are subject to metabolism, estimates for rates of conversion should be included when modeling bioaccumulation, breakdown, and flux from sediment reservoirs. Even among the invertebrates who are not generally expected to metabolize PAHs at rates comparable to higher vertebrates, body burdens of PAH metabolites may be significant, exceeding levels of parent PAH in edible tissues. Impacts of dietary exposure to PAH metabolites on aquatic species need to be assessed.

Future studies should focus on the behavior of specific PAH compounds in harbor sediments and the unique aspects of highly contaminated sites with respect to PAH flux, degradation and bioavailability. The high flux of partially metabolized PAHs from Fort Pt. Channel demonstrated in our work suggests that something different is going on at this site. Sediments from this site have also been observed by Chin and Gschwend (1992) to have relatively high sorption coefficients for the PAH pyrene larger than would be predicted based on simple partitioning. Chin and Gschwend suggested that colloidal material at Fort Point Channel may serve to enrich the concentration of higher molecular weight organics such as PAHs in pore waters where they would be available for remobilization by bioirrigation. McGroddy (1993) also noted significantly increased levels of PAH-bound colloids and PAH in the porewaters of Fort Point Channel sediments as compared to other sites in Boston Harbor in her detailed analysis of PAH partitioning in sediments from Boston Harbor. The interaction of geochemical and microbial processes in influencing PAH availability and trophic transfer needs to be further addressed.

Specific management issues that must be addressed, especially in consideration of the ecological and human health risks associated with PAH contamination, are the development of PAH guidelines for benthic habitats. These should include consideration of guidelines for the disposal of PAH-contaminated dredged materials, further development of interim

sediment criteria, and the determination of concentrations of PAH and/or PAH-metabolites in commercially important resource species.

References:

Cahill, J. and K. Imbalzano. 1991. An inventory of organic and metal contamination in Massachusetts Bay, Cape Cod Bay, and Boston Harbor sediments and assessment of regional sediment quality. EPA 171-R-92-013.

Chin, Y.-P. and P.M. Gschwend. 1992. Partitioning of polycyclic aromatic hydrocarbons to porewater organic colloids. Environmental Science and Technology 26:1621-1626.

MacDonald, D.A. 1991. Status and trends in concentrations of selected contaminants in Boston Harbor sediments and biota. NOAA Technical Memorandum NOS OMA 56, Seattle, WA.

McGroddy, S.E. 1993. Sediment-Porewater Partitioning of PAHs and PCBs in Boston Harbor, Mass. Ph.D. Dissertation, Environmental Sciences Program, Universityof Massachusetts-Boston.

Menzie-Cura & Associates, Inc. 1991. Sources and loadings of pollutants to the Massachusetts Bays. Report to the Massachusetts Bays Program, MBP-91-01, Boston, MA.

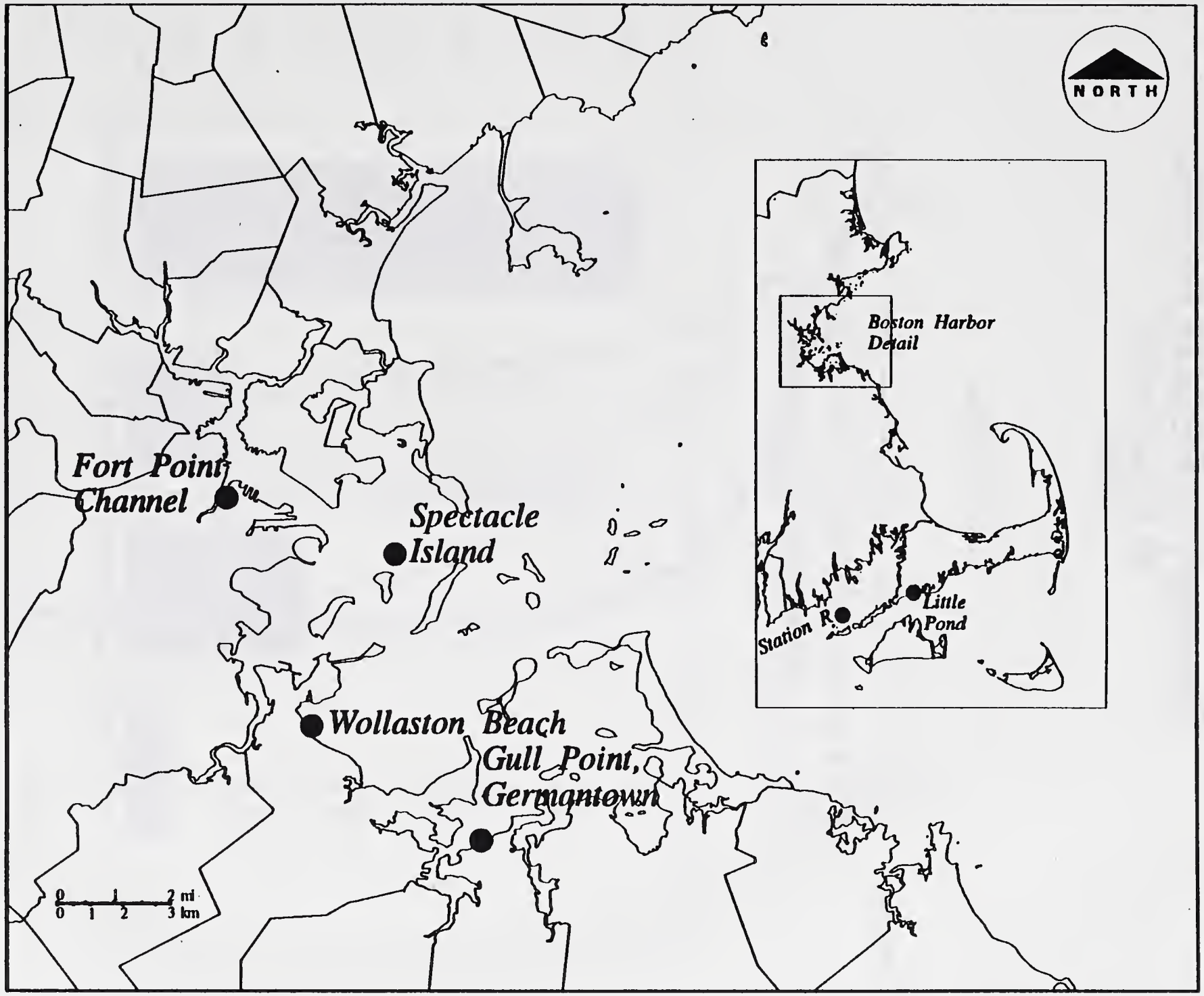

Figure 1. Location of Sample Sites

Figure 2

Summary of REDOX Profiles
All Experiments

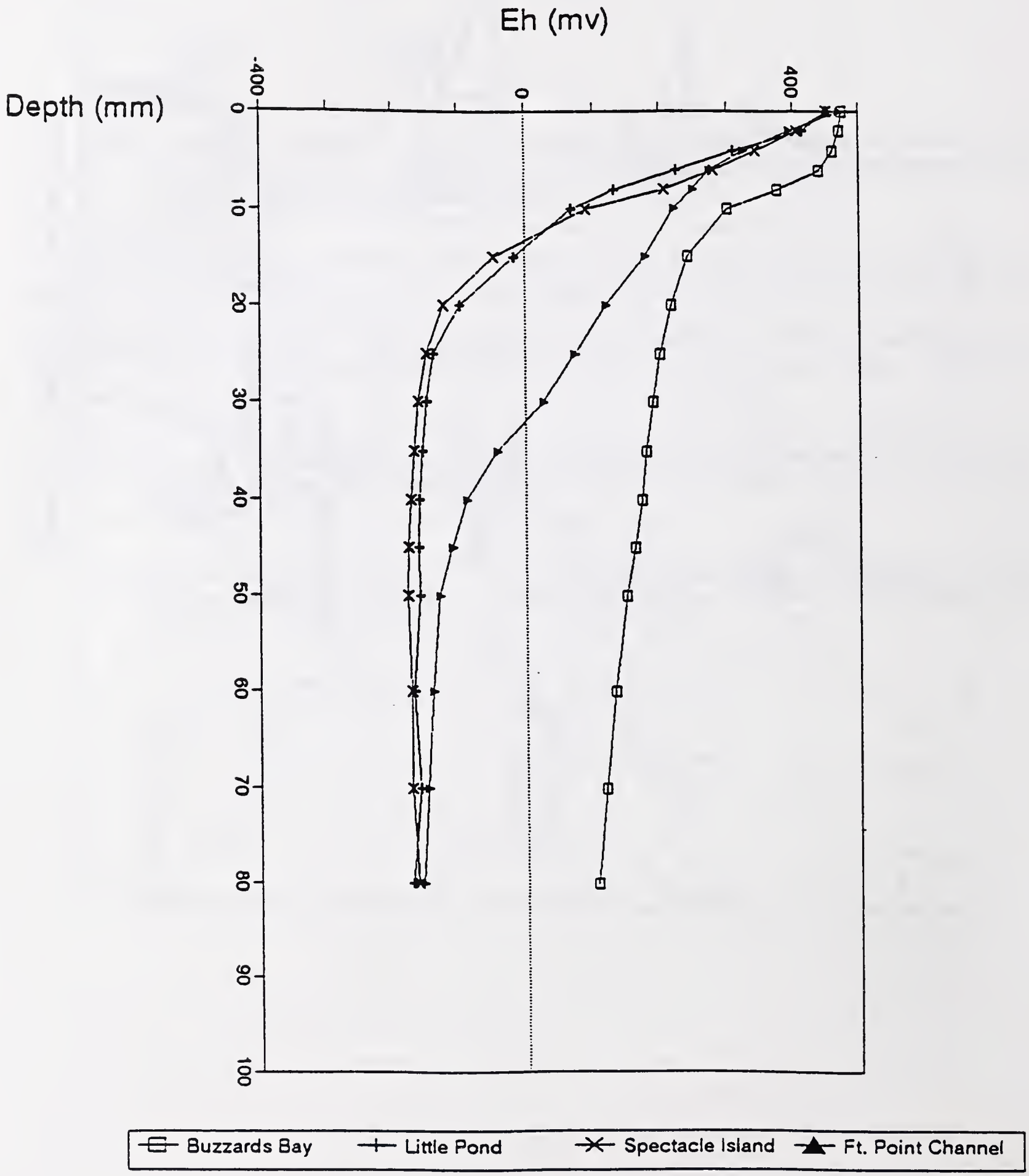

Figure 3

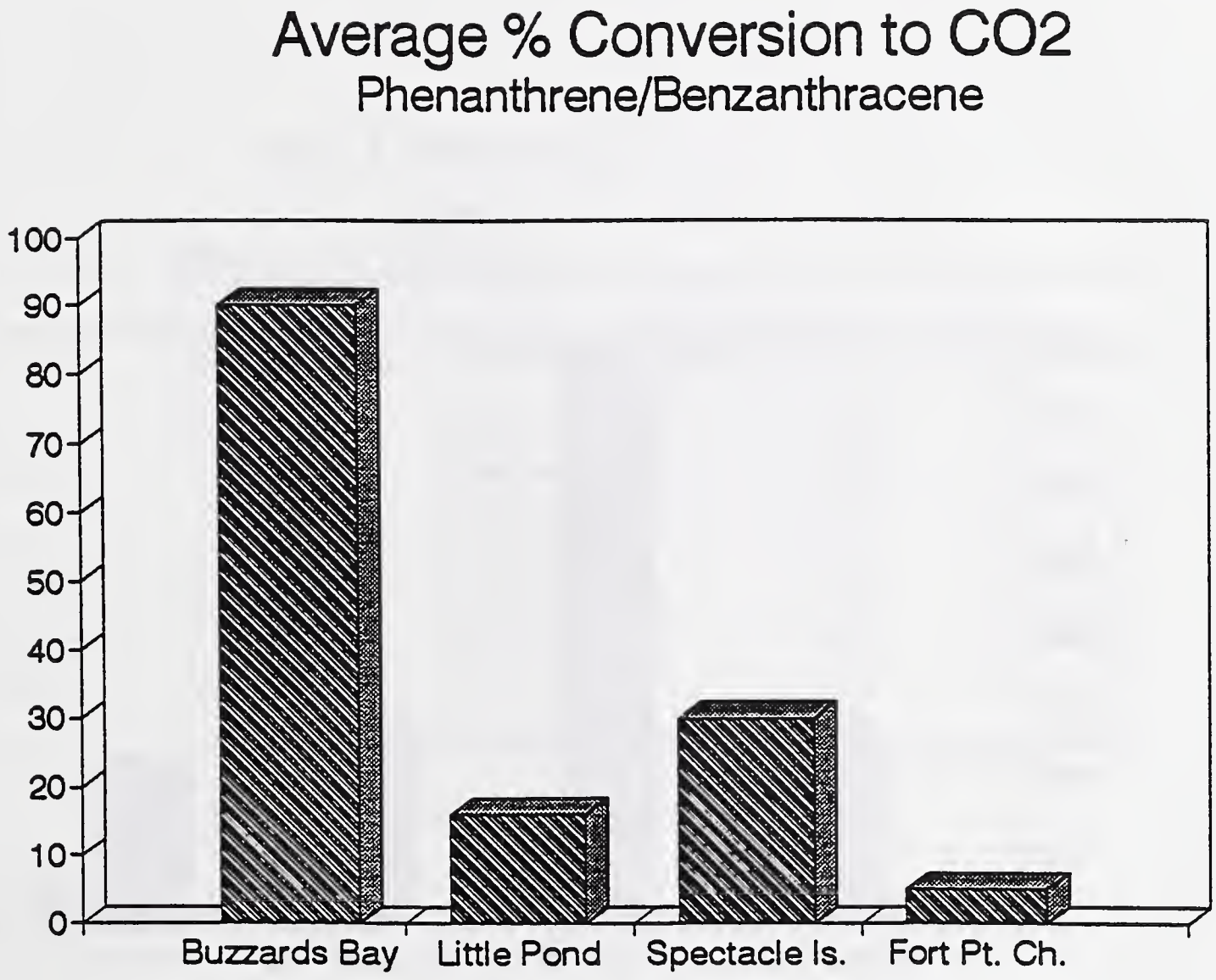
Average % Conversion to CO2
Phenanthrene/Benzanthracene
100
90
80
70
60
50
40
30
20
10
0
Buzzards Bay
Little Pond
Spectacle Is.
Fort Pt. Ch.

Figure 4

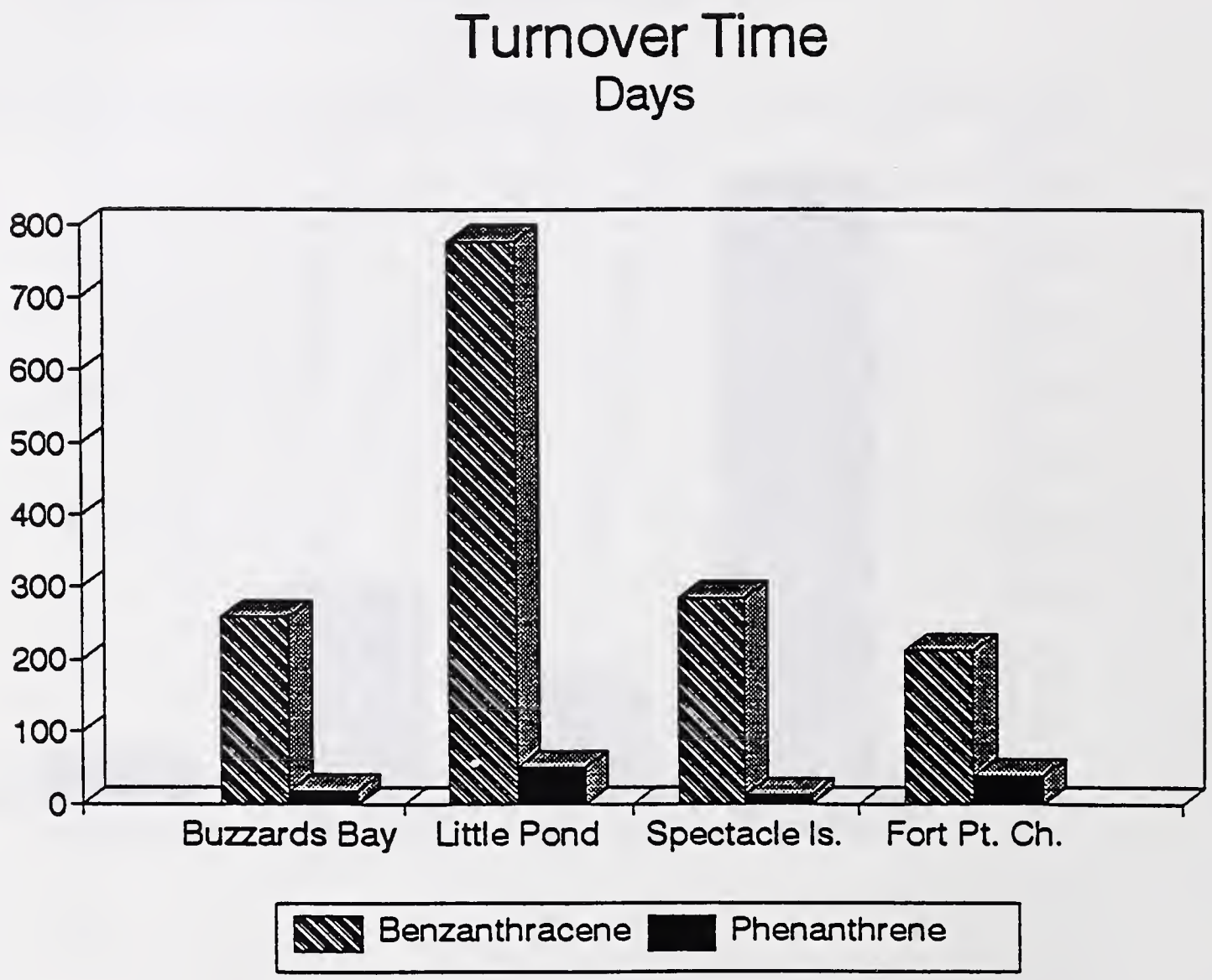
Turnover Time
Days
800
700
600
500
400
300
200
100
0
Buzzards Bay
Little Pond
Spectacle Is.
Fort Pt. Ch.
Benzanthracene
Phenanthrene

Table 1

Bioaccumulation Factors

Sediment Type	Organism	Benzanthracene	Phenanthrene
Buzzards Bay	S.viridis	2.22	0.44
	M.arenaria	0.06	0.02
Little Pond	S.viridis	2.72	1.95
	M.arenaria	0.11	0.1
Spectacle Is.	S.viridis	0.44	0.47
	M.arenaria	0.04	0.08
Fort Pt. Ch.	S.viridis	0.93	0.63
	M.arenaria	0.04	0.04

bioaccumulation factor=(nmol/glw)/(nmol/goc)